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Accounting for optical errors in microtensiometry

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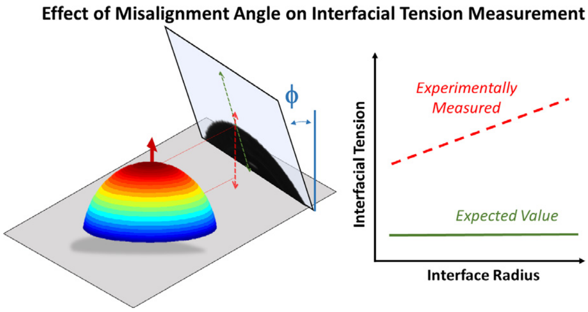
GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: Drop shape analysis (DSA) techniques measure interfacial tension subject to error in image analysis and the optical system. While considerable efforts have been made to minimize image analysis errors, very little work has treated optical errors. There are two main sources of error when considering the optical system: the angle of misalignment and the choice of focal plane. Due to the convoluted nature of these sources, small angles of misalignment can lead to large errors in measured curvature. We demonstrate using microtensiometry the contributions of these sources to measured errors in radius, and, more importantly, deconvolute the effects of misalignment and focal plane. Our findings are expected to have broad implications on all optical techniques measuring interfacial curvature.
Experiments: A geometric model is developed to analytically determine the contributions of misalignment angle and choice of focal plane on measurement error for spherical cap interfaces. This work utilizes a microtensiometer to validate the geometric model and to quantify the effect of both sources of error. For the case of a microtensiometer, an empirical calibration is demonstrated that corrects for optical errors and drastically simplifies implementation.
Findings: The combination of geometric modeling and experimental results reveal a convoluted relationship between the true and measured interfacial radius as a function of the misalignment angle and choice of focal plane. The validated geometric model produces a full operating window that is strongly dependent on the capillary radius and spherical cap height. In all cases, the contribution of optical errors is minimized when the height of the spherical cap is equivalent to the capillary radius, i.e. a hemispherical interface. The understanding of these errors allow for correct measure of interfacial curvature and interfacial tension regardless of experimental setup. For the case of microtensiometry, this greatly decreases the time for experimental setup and increases experiential accuracy. In a broad sense, this work outlines the importance of optical errors in all DSA techniques. More specifically, these results have important implications for all microscale and microfluidic measurements of interface curvature.

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1. Introduction

The ability of a surfactant to lower the interfacial tension of a fluid-fluid interface is crucial to a large variety of applications in industrial processes.[1] Measuring the dynamic interfacial tension of surfactant solutions gives rise to fundamental understanding of surfactant transport and equilibrium interfacial behavior. Quantification of dynamic interfacial phenomena have important implications in various applications [1] such as: emulsion stability [2,3], the fluid mechanics of drops [4,5], predicting mass transfer [6–8], design of microfluidics [9,10], coatings [11–13], film drainage [14,15], interfacial rheology [16–19], surfactant performance [20–22], etc. Existing and novel applications necessitate our understanding of the roles of thermodynamics, diffusion, and kinetics in the efficacy of surfactants in industrial systems.

Dynamic interfacial tension is best quantified using methods employing drop shape analysis (DSA) techniques. This is typically referred to as the pendant drop method for millimeter sized drops or bubbles [20,23–26]. Several novel DSA techniques have been developed that utilize microscale DSA to measure interfacial tension [27–32]. Specifically, the microtensiometer of Alvarez et al. is ideal for measuring dynamic interfacial tensions with minimal experimental time, low sample volumes, and direct measurement and control of Laplace pressure and radius of curvature. Additionally, this method is superior to pendant drop for measuring interfacial rheology and other dynamic interfaces because of the simplicity of calculating interfacial area [19,33–35]. Common to all of these methods is the use of image analysis to obtain a value of interfacial tension as a function of time. The pendant drop method uses a fit to an interfacial profile utilizing the Young-Laplace equation $\gamma = \Delta P/2H$, where $2H$ is the drop's curvature and ΔP is approximated as the hydrostatic pressure [36,37]. Microtensiometry simplifies DSA by (i) utilizing spherical drops or bubbles and (ii) directly measuring ΔP. The error in measured curvature from both methods is strongly dependent on the optical system. To account for this, many users typically attempt painstaking efforts to perfectly orient and focus their systems, often with only limited success [23,38–41]. Furthermore, the effect of misalignment has not been accounted for in several attempts to bound the validity of experimental techniques, which could strongly influence their conclusions [42–48].

There are two primary sources of error coming from the optical system: imaging misalignment and choice of focal plane. All DSA techniques require the projection of a 3D drop shape onto a 2D image plane. This projected image is known as the perspective projection and depends on the relative orientation of the object in space to that of the image plane [49–52]. Utilization of the Young-Laplace equation assumes an orthographic projection, see Fig. 1, whereby the image plane is parallel to an axisymmetric plane of the drop [36,37,53]. In a real experiment, there is some angle of misalignment in the optical path that results in a axonometric projection of the drop interface. This projection does not preserve radius of curvature and therefore results in a measurement error of the interfacial tension. Moreover, the choice of focal plane produces a unique perspective projection that does not necessarily capture the curvature of interest. The focal plane is user dependent and a function of the numerical aperture, the field of view, and other characteristic features of the objective/lens [54,55,52]. Correcting for misalignment and focal plane necessitates a perspective transformation to recreate the orthographic projection from the perspective projection [49,50]. This requires determining the global spatial coordinates between the drop and the image plane at all times [55]. This is an expensive exercise when considering the number of experiments required to develop adsorption isotherms and the times required to measure transport of surfactants.

In this work we determine the effect of both misalignment and focal plane on the measured radius of curvature for spherical microscale interfaces. The analysis is performed using a geometric model to simulate the perspective projection one would obtain in an experiment for a given misalignment angle, ϕ, and a relative focal plane, ζ. The model is validated against experimental data measured on a microtensiometer [27]. This knowledge leads to an operating window whereby a perspective transformation in space and time reduces to a simple correction of the measured radius. While the current implementation of microscale DSA techniques require painstaking system alignment and very careful focusing to reduce error, we show that the use of the simple correction eliminates the need for these efforts. Furthermore, more complex measurements of interfacial phenomena (e.g. closed systems, expanding/contracting interfaces) require experimental apparatuses that are off-microscope or that are extremely sensitive to dynamics, necessitating further attention on alignment and focus. Our goal is to reduce the complexity of microscale DSA techniques to facilitate inexpensive, accurate, low volume, and fast measurement of fundamental interfacial phenomena regardless of experimental apparatus. Additionally, the analysis of errors presented here provides the most robust potential framework for mitigation of errors in typical DSA techniques containing multiple radii of curvature.

2. Experimental section

The microtensiometer [27] design is based on the original design of Alvarez et al. The cell is constructed of a single piece of ABS plastic that was 3D-printed. The micro-pipettes used for this study were nominally 10, 30, and 200 μm in diameter at the tip which tapers down from a 1 mm glass capillary, obtained from World Precision Instruments (*Sarasota, FL*) with the exception of the 200 μm capillary which was pulled as described in the original work. Clean, dry air was supplied and pressure controlled via a Fluigent microfluidics controller (MFCS-100, *Lowell, MA*) and measured using a well calibrated, highly accurate pressure transducer (Omega PX409-XL, *Stamford, CT*). The interface is imaged using an inverted microscope (Nikon Instruments Eclipse TE 2000-S, *Melville, NY*) equipped with a high frame-rate camera (Point Grey Grasshopper 3, *Richmond, BC, Canada*) and Nikon Plan Fluor objectives (10×, 20×, 50×). For measurements of 200 μm capillaries the 10× objective (N.A. = 0.30) was used, for 30 μm the 20× (N.A. = 0.45) objective was used, and for 10 μm the 50× (N.A. = 0.45) objective was used. The microtensiometer is attached to the microscope using a custom 3D-printed stage. The control and data acquisition schemes are implemented using software written in LabVIEW (National Instruments, *Austin, TX*). Spherical cap radius measurements were made at the air-water (pure), air-methanol, and air-ethylene glycol surfaces at 25 °C. Measurements at the air-water surface were used to validate the geometric model. Measurements at the air-methanol and air-ethylene glycol surfaces were used to validate the calibration experiments.

The working principle of the microtensiometer is to measure the interface curvature from a perspective projection via a fit of a circle, with radius R, and measure the pressure via a gauge transducer inside the capillary. Since gravity has little effect on the drop shape, the Young-Laplace equation reduces to the Laplace equation given by $\Delta P = 2\gamma/R$. The radius is measured as a function of time using a LabVIEW circular gradient based algorithm fit [27]. For some results, independent ImageJ [56] measurements were used

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[1] Distinction is typically made between surface tension, gas-liquid, and interfacial tension, liquid-liquid. In this work, we use the words interfacial tension to denote in general any fluid-fluid interface.